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A vectorizable second-order MCSCF method is first outlined and then shown to yield a unified framework from which to develop MCSCF and multi-reference CI energy derivatives. Non-adiabatic coupling matrix elements can be extracted from this framework by using a common orbital set to describe both states. CI non-adiabatic coupling matrix elements are simply obtained by employing transition density matrices in the multi-reference CI gradient program.

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TECHNICAL REPORT BRL-TR-2735

A UNIFIED TREATMENT OF ENERGY DERIVATIVES AND NON-ADIABATIC COUPLING MATRIX ELEMENTS

Byron H. Lengsfield, III

June 1986

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I. INTRODUCTION

The calculation of non-adiabatic coupling matrix elements between adiabatic states has traditionally been a very difficult problem. Recent studies have relied on the existence of a compact diabatic or pseudo-diabatic basis, or on finite difference methods. We have recently proposed an analytical method of obtaining first-order non-adiabatic coupling matrix elements (NACMEs). In our approach we employ a state-averaged MCSCF procedure to define a common orbital basis. With a few simple modifications we are then able to make use of the machinery developed to calculate CI gradients and MCSCF second derivatives to obtain the desired quantities. In fact, the methods employed to obtain MCSCF wavefunctions, MCSCF second derivatives, multi-reference CI gradients and NACMEs can be cast into one unified and compact framework.

It is the purpose of this manuscript to outline the methods used to obtain energy derivatives and NACMEs. The first section will be devoted to an outline of the second-order MCSCF procedure employed in the ALCHEMY II program package. In the second section, we show how MCSCF derivatives can be fit neatly into this package and finally, we show that analytical NACMEs can be obtained within this framework if a common orbital set is used to describe both states.

A. Second-Order MCSCF Methodology

In this section, we outline the second-order MCSCF method employed in the ALCHEMY II series of programs.[1] The construction of the orbital hessian is completely vectorizable and requires no formula tape. The CI variations are handled directly in the CSF basis, so that large CI expansions can be addressed. Many of the matrices constructed as precursors to the orbital hessian are retained and used to construct the orbital contribution to the inhomogenious portion of the coupled-perturbed MCSCF (CP-MCSCF) equations. Similiarly, the code employed to directly compute the result of multiplying the CI-orbital coupling portion of the MCSCF hessian times a trial vector is used to construct the CI contribution to the inhomogeneous portion of the CP-MCSCF equations.

In the discussions which follow, I, J, K, L will be used to denote inactive orbitals, A, B, C, D will be used to denote active orbitals, R, S, T, U will be used to denote any orbital in either the inactive, active, or virtual spaces, and a, b, c, d, will be used to denote atomic orbitals. The wavefunction will be represented as follows,

$$\psi = \sum_p C_p \phi_p \tag{1}$$

where ϕ represents our CSF basis and C_i is an element of the CI vector. The energy expression is partitioned into an inactive portion, an inactive-active portion, and a purely active portion.[2]

$$E = \sum_I 2h_{II} + \sum_{IJ} (2 J_{JJ}^{II} - K_{JJ}^{II})$$

$$+ \sum_I \sum_{AB} D_{AB} \left(2 J_{II}^{AB} - \frac{1}{2} \{ K_{II}^{AB} + K_{II}^{BA} \} \right) \qquad (2)$$

$$+ \sum_{AB} D_{AB} h_{AB} + \sum_{ABCD} D_{ABCD} J_{CD}^{AB}$$

$$= \langle C | H | C \rangle$$

where

$$h_{TU} = \langle T | \tilde{h} | U \rangle,$$

$$J_{TU}^{RS} = \langle RS | \tilde{g} | TU \rangle,$$

$$K_{TU}^{RS} = \langle RT | \tilde{g} | SU \rangle,$$

$$D_{AB} = \sum_{pq} C_p \, k_{pq}^{AB} \, C_q$$

and

$$D_{ABCD} = \sum_{pq} C_p \, k_{pq}^{ABCD} \, C_q$$

k_{pq}^{AB} and k_{pq}^{ABCD} are spin-coupling constants. $\tilde{h}$ and $\tilde{g}$ are the usual one and two electron operators appearing in the Born-Oppenheimer hamiltonian. D_{AB} and D_{ABCD} are the elements of the one and two-particle density matrix respectively. Unitary orbital variations are introduced by means of an exponential operator containing only non-redundant terms,[3,4]

$$U = e^{-\Delta} = 1 - \Delta + \frac{1}{2} \Delta^2 + \ldots$$

$$= U_o + U_1 + U_2 + \ldots \qquad (3)$$

The elements of Δ are our variational parameters. The energy expression is expanded to second-order in Δ and then differentiated. First-order variations and second-order terms arising from U_2 are obtained by constructing a Lagrangian matrix,[5,6]

$$L_{TA} = 2 \{ \sum_B D_{AB} h_{TB} + 2 \sum_{BCD} D_{ABCD} J_{TB}^{CD} \} \qquad (4)$$

Second-order terms arising from simultaneous first-order variations are obtained by first constructing a Y matrix.[1,5-8]

$$Y_{(AT)(BS)} = d_{AB}^h \, h_{TS} + \sum d_{ABCD}^J \, J_{TS}^{CD}$$

$$+ \sum_{CD} (d_{ABCD}^K \, K_{TS}^{CD} + d_{ABCD}^{K^+} \, K_{TS}^{DC}) \qquad (5)$$

$$= Y_{TS}^{AB}$$

$$= \tilde{Y}^{AB}, \text{ for all } T, S$$

here d^h_{AB} and d^J_{ABCD} are scaled elements of the one and two-particle density matrix. The scaling factor depends only on the symmetry of the indices of the density matrix elements, (whether $A=B$, $C=D$, or $AB=CD$). Similiarly, d^K_{ABCD} is generated by scaling the D_{ACBD} density matrix element. It is important to note that the one-electron and coulomb contributions to the Y matrix, Y^J, can be contracted and used to construct the Lagrangian.[1][5-8] The Y matrix and the Lagrangian are constructed by multiplying a scaled density element times a coulomb or exchange matrix, a procedure which is readily vectorizable.

The Y matrix is partitioned into inactive-inactive, inactive-active, and active-active blocks. The inactive-inactive block can be constructed by weighting the coulomb and exchange matrices with a small number of constants. For example, an off-diagonal matrix in the inactive-inactive sub-block of the Y matrix is constructed from only three terms,

$$Y^{IJ}_{TS} = a_{IJ} J^{IJ}_{TS} + b_{IJ} K^{IJ}_{TS} + b^+_{IJ} K^{JI}_{TS}. \tag{6}$$

The inactive-active portion of the Y matrix requires only scaled one-particle density matrix elements.

$$Y^{AI}_{TS} = \sum_B (d^J_{AB} J^{BI}_{TS} + d^K_{AB} K^{BI}_{TS} + d^{K^+}_{AB} K^{IB}_{TS}) \tag{7}$$

The partitioning of the Y matrix is computationally attractive as it reduces the number of matrices which need to be held in core at one time. In addition, it provides the flexibility of computing the inactive-inactive sub-block or the inactive-active sub-block directly as discussed by Bacskay[9] and Olsen, et al.,[10] respectively. In addition, the occupied-virtual, occupied-virtual portions of the matrix can be combined with Lagrangian contributions to generate an occupied-virtual, occupied-virtual sub-blocks of the orbital hessian, which need not be kept in core.

The construction of the orbital hessian proceeds as follows,

(1) A reduced integral transformation is used to form the J and K matrices in the ao basis and to calculate the integrals needed to perform the CI,

(2) In a two step MCSCF procedure the CI calculation is then carried out,

(3) The CI vector is used to construct the unique elements of the one and two-particle density matrix over the active orbitals,

(4) The density matrix elements are scaled and reordered in the case of exchange contributions,

(5) The coulomb and fock operator contributions to the Y matrix are generated,

(6) The Y matrix is contracted with the molecular orbitals to produce the active portion of the Lagrangian. The inactive portion of the Lagrangian is generated from fock matrices,

(7) The exchange contributions are added to the Y matrix, and

(8) The Lagrangian is folded to produce the MCSCF orbital gradient (g_{AB} = L_{AB} - L_{BA}) and the Y matrix is transformed to the mo basis, similarly folded and combined with Lagrangian contributions to produce the MCSCF hessian.

The Newton-Raphson linear equations are solved iteratively,

$$\begin{pmatrix} \dfrac{\partial^2 E}{\partial O^2} & \dfrac{\partial^2 E}{\partial O \partial C} \\[3ex] \dfrac{\partial^2 E}{\partial C \partial O} & \dfrac{\partial^2 E}{\partial C^2} \end{pmatrix} \begin{pmatrix} \delta O \\[3ex] \delta C \end{pmatrix} = \begin{pmatrix} -g_O \\[3ex] -g_C \end{pmatrix} \tag{8}$$

where δO and δC represent orbital and CI variations, respectively, and the remaining portions of the MCSCF hessian are treated directly.[11][12] The second-order CI terms are handled with a direct-CI program.

Multiplication of the CI-orbital portion of the hessian times a trial vector are re-expressed as a gradient constructed with transition density matrices,[12]

$$\left(\frac{\partial^2 E}{\partial O \partial C}\right) \delta C = g_O^{\delta C} \tag{9}$$

or updated integrals,[12]

$$\left(\frac{\partial^2 E}{\partial C \partial O}\right) \delta O = g_C^{\delta O} = (H-E)^{\delta O}|C\rangle . \tag{10}$$

The updated integrals used to construct $g_C^{\delta O}$ are obtained as follows,

$$\langle ABCD \rangle^{\delta O} = \sum_T (\delta O_{TA} \langle TBCD \rangle + \delta O_{TB} \langle ATCD \rangle \tag{11}$$
$$+ \delta O_{TC} \langle ABTD \rangle + \delta O_{TD} \langle ABCT \rangle)$$

where $\langle TBCD \rangle \equiv \langle TB | \tilde{g} | CD \rangle$. The integrals with three indices transformed $\langle TBCD \rangle$, etc., have been generated earlier by contracting a coulomb matrix.

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II. MCSCF SECOND-DERIVATIVES

The formalism needed to generate a MCSCF force constant matrix has been discussed by a number of authors.[6,13-16] The method presented by Page, et al.,[15] has been incorporated in the MCSCF framework discussed above as it seems to offer a number of computational advantages. In particular, the construction of the inhomogeneity in the CP-MCSCF equations,

$$\begin{pmatrix} \dfrac{\partial^2 E}{\partial O^2} & \dfrac{\partial^2 E}{\partial O \partial C} \\ \\ \dfrac{\partial^2 E}{\partial C \partial O} & \dfrac{\partial^2 E}{\partial C^2} \end{pmatrix} \begin{pmatrix} \delta O^\alpha \\ \\ \delta C^\alpha \end{pmatrix} = \begin{pmatrix} -g_O^\alpha - g_O^{T\alpha} \\ \\ -g_C^\alpha - g_C^{T\alpha} \end{pmatrix} \tag{12}$$

involves the same code employed in the construction of the MCSCF Lagrangian and in the handling of the CI-orbital coupling terms in the direct solution to the Newton-Raphson equations. In this formalism, g_O^α and g_C^α are the orbital and CI gradients constructed with derivative ao integrals. Similiarly, $g_O^{T\alpha}$ and $g_C^{T\alpha}$ are gradients constructed with updated integrals where one index has been transformed with the T^α matrix. T^α is an upper triangular matrix constructed from transforming the derivative ao overlap integrals into the mo basis,

$$T_{RS}^\alpha = - S_{RS}^\alpha \; , \; S > R$$

$$T_{RR}^\alpha = - \frac{1}{2} S_{RR}^\alpha \tag{13}$$

and

$$T_{SR} = 0, \; S > R$$

$g_O^{T\alpha}$ is generated by contracting the Y matrix with T^α and transforming the MCSCF Lagrangian with T^α, to first produce the T^α Lagrangian, $L^{T\alpha}$.

$$L_{RA}^{T\alpha} = \sum_{MS} Y_{RS}^{AM} T_{SM}^\alpha + \sum_S T_{SR}^\alpha L_{SA} \tag{14}$$

where the summation over M runs over all occupied orbitals. The code employed in the MCSCF program to produce the Lagrangian from Y^J is also used at this point to contract the Y matrix.

$g_C^{T\alpha}$ is obtained from the code employed in the direct solution of the Newton-Raphson equations to construct $g_C^{\delta O}$. In this case the updated integrals are obtained by contracting the partially transformed integrals, $\langle TBCD \rangle$, etc., with the T^α matrix.

The final expression for the first and second derivatives of the MCSCF energy expressions are,[15]

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$$E^{\alpha} = \sum_{ab} D_{ab} h^{\alpha}_{ab} + \sum_{abcd} D_{abcd}\, g^{\alpha}_{abcd} + \sum_{TA} L_{TA} T^{\alpha}_{TA} \qquad (15)$$

and

$$E^{\alpha\beta} = 2 \langle C^{\beta} | H^{\alpha} + H^{T\alpha} | C \rangle +$$

$$\sum_{ab} D_{ab} h^{\alpha\beta}_{ab} + \sum_{abcd} D_{abcd}\, g^{\alpha\beta}_{abcd} + \sum_{TA} L^{\beta}_{TA} T^{\alpha}_{TA} + \qquad (16)$$

$$\sum_{TA} (L^{\alpha} + L^{T\alpha})_{TA}\, U^{\beta}_{TA} + \sum_{AB} L_{AB} [T^{\alpha\beta}_{AB} + \sum_{S} (T^{\alpha}_{SA} T^{\beta}_{SB} + T^{\alpha}_{SA} T^{\beta}_{BS})]$$

where U^{β} is the derivative of the mo coefficient matrix obtained by combining
the solution of the CP-MCSCF equations and T^{β}. These equations only employ
quantities (L^{α} and $L^{T\alpha}$) used to construct the inhomogeneity in the CP-MCSCF
equations, the solution to the CP-MCSCF equations themselves or terms
generated from a SCF derivative package after the MCSCF density matrix has
been transformed to the ao basis. The actual assemblage of the MCSCF force-
constant matrix, after the solution the CP-MCSCF equations and the contraction
of the derivative ao integrals with ao density matrix, is extremely simple.

III. NON-ADIABATIC COUPLING MATRIX ELEMENTS

The first-order non-adiabatic coupling matrix element,[17-19] (NACME),

$$D_{(M,N;\alpha)} = \langle \psi_M | \frac{d}{d\alpha} \psi_N \rangle = \langle \psi_M | \psi^{(\alpha)}_N \rangle \qquad (17)$$

can be calculated in a straightforward manner if the same orbital basis is
used to represent the two states.[20][21] In this case, the required
wavefunction derivatives are obtained from a state-averaged CP-MCSCF equation.
The NACME is broken down into two terms,

$$D_{(M,N,\alpha)} = D_C + D_O$$

$$= \langle C_M | C^{\alpha}_N \rangle + \sum_{ST} D^{M,N}_{ST} (U^{\alpha}_{ST} + V^{\alpha}_{ST}) . \qquad (18)$$

The first term is simply the overlap of a CI vector and a derivative CI
vector. For a MCSCF wavefunction, C^{α}_N is obtained from the solution to the CP-
MCSCF equations, so this term poses no new problems. For a CI wavefunction,
the direct evaluation of this term would require the solution of at least one
CP-CI type of equation,

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$$(H - E_M) \, C_M^\alpha = - (H - E_M)^{(\alpha)} C_M \, . \tag{19}$$

Multiplying Eq. 19 on the left by C_N, we find the usual perturbation expression,[21]

$$\langle C_N | C_M^\alpha \rangle = (E_M - E_N)^{-1} \langle C_N | H^{(\alpha)} | C_M \rangle \, . \tag{20}$$

The term on the right-hand-side of this equation is a familiar one. It is similar to the expression for a CI gradient. The only difference is that we need to employ transition density matrices in place of normal density matrices in our equations. The formal expression for a CI gradient is[22]

$$E_M^{(\alpha)} = \sum_{ab} D_{ab}^{M,M} h_{ab}^\alpha + \sum_{abcd} D_{abcd}^{M,M} g_{abcd}^\alpha + \sum_{TS} L_{TS}^{M,M} U_{TS}^\alpha \tag{21}$$

$$= \langle C_M | H^{(\alpha)} | C_M \rangle \, .$$

The first term is the trace of the density matrix with derivative ao integrals, while the second term is the contraction of the CI Lagrangian with the derivative of the mo coefficients. Thus,[21]

$$D_C = (E_M - E_N)^{-1} \{ \sum_{ab} D_{ab}^{M,N} h_{ab}^\alpha + \sum_{abcd} D_{abcd}^{M,N} g_{abcd}^\alpha + \sum_{TS} L_{TS}^{M,N} U_{TS}^\alpha \} \, . \tag{22}$$

Therefore, we able to make use of the same code used to compute CI gradients.

In the expression for the orbital contribution to the first-order NACME we are dealing with a one-electron operator so the resulting expression involves the trace of an one-particle density matrix and an overlap term,[20]

$$D_O = \sum_{ST} D_{S,T}^{M,N} (U_{S,T}^\alpha + V_{S,T}^\alpha) \tag{23}$$

$D_{S,T}^{M,N}$ is an element of a non-symmetric, one-particle transition density matrix. $U_{S,T}^\alpha$ is the derivative of the mo coefficients obtained from the solution to the state-average CP-MCSCF equations, and $V_{S,T}^\alpha$ is obtained by transforming half-derivative ao overlap integrals into the mo basis. Two overlap terms are needed as the derivative of the molecular orbitals are expressed as,[20]

$$\frac{dO}{d\alpha} = \frac{d}{d\alpha} (xt) = x^\alpha t + x t^\alpha$$

$$= x^\alpha t + O U^\alpha \tag{24}$$

where O are the molecular orbitals, x is a vector of atomic orbitals, and t is the mo coefficient matrix.[20]

$$V^\alpha_{ST} = \sum_{ab} t_{aS} \langle x_a | x^\alpha_b \rangle t_{bT} \qquad (25)$$

and $\langle x_a | x^\alpha_b \rangle$ is a half-derivative overlap integral.

The new terms required to compute a NACME are a square one-particle transition matrix and half-derivative ao overlap integrals. The CI gradient package must also be modified to produce the required one and two-particle transition density matrices, while the MCSCF package need only be modified to compute a square one-particle transition density matrix.

This formalism can be extended to analytically compute second-order NACMEs. This requires the set-up of the second-order state-averaged CP-MCSCF equations and the code to compute a square two-particle transition density matrix. A second-order CI NACME would require the solution of the first-order CP-CI equations.

IV. CONCLUSION

A unified treatment of energy derivatives and non-adiabatic coupling matrix elements has been outlined. We showed that in the case of both energy derivatives and NACMEs the final equations could be rewritten in a form that resulted in the efficient use of existing MCSCF or derivative methods.

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